Ionizing Radiation Effect of HDPE Measured by Nano-hardness

Martin Ovsik[1,a], David Manas[1,b], Miroslav Manas[1,c] , Michal Stanek[1,d], Martin Bednarik[1,e], Petr Krátký[1,f].

[1]Tomas Bata University in Zlin, TGM 5555, 760 01 Zlin, Czech Republic

[a]ovsik@ft.utb.cz, [b]dmanas@ft.utb.cz, [c]manas@ft.utb.cz, [d]stanek@ft.utb.cz, [e]mbednarik@ft.utb.cz, [f]kratky@ft.utb.cz

Keywords: High-density polyethylene, Ionizing radiation, cross - linking, Nano - hardness, Depth Sensing Indentation.

Abstract: This article deals with the influence of different doses of Beta radiation on nano-mechanical properties of High-density polyethylene (HDPE). These nano-mechanical properties were measured by the Depth Sensing Indentation - DSI method on samples which were non-irradiated and irradiated by different doses of the β - radiation. The highest values of nano-mechanical properties were reached at radiation dose of 99 kGy, when the nano-hardness values increased by about 23%. The purpose of the article is to consider to what extent the irradiation process influences the resulting nano-mechanical properties measured by the Depth Sensing Indentation method.

Introduction

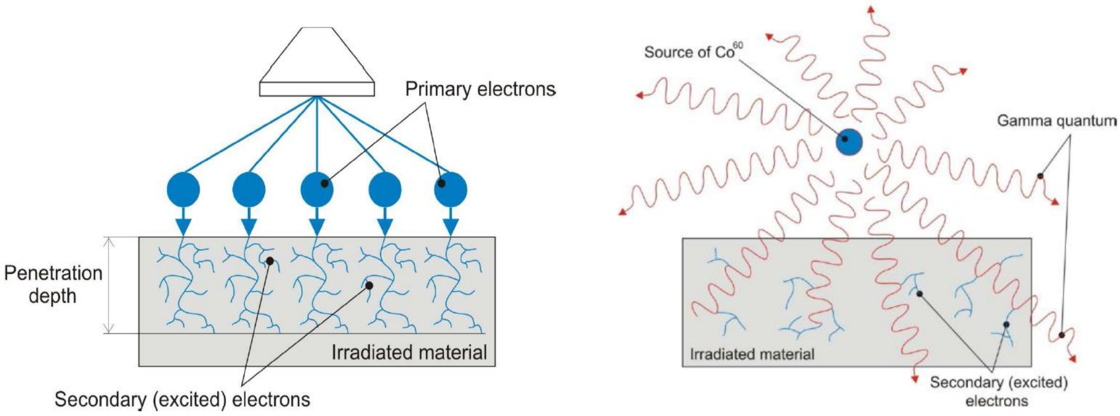
A linear polymer, High Density Polyethylene (HDPE) is prepared from ethylene by a catalytic process. The absence of branching results in a more closely packed structure with a higher density and somewhat higher chemical resistance than LDPE. HDPE is also somewhat harder and more opaque and it can withstand rather higher temperatures (120° Celsius for short periods, 110° Celsius continuously. [1]

High density linear polyethylene (HDPE) contains one terminal vinyl group per molecule. At low radiation doses, this vinyl group has the effect of increasing the molecular weight of the HDPE by the chain formation of Y-links between the vinyl and the secondary alkyl radicals produced by the radiation. At ambient temperatures, polyethylene is always in the semicrystalline form. The cross-linking takes place mainly in the amorphous region and the interface between the two phases. The cores of the crystalline regions sustain radiation-induced transvinylene formation in proportion to their weight fraction, but they are scarcely involved in gel formation. [1-2]

The effects of ionizing radiation on polyethylene in all its forms can be summarized as follows: [1-2]

- The evolution of hydrogen.
- The formation of carbon-carbon cross-links.
- An increase in unsaturation to an equilibrium level.
- A reduction in crystallinity.
- The formation of color bodies in the resin.
- Surface oxidation during irradiation in air.

Crosslinking is a process in which polymer chains are associated through chemical bonds. Crosslinking is carried out by chemical reactions or radiation and in most cases the process is irreversible. Ionizing radiation includes high-energy electrons (electron beam - β-rays) (Fig. 1 a) and gamma rays (γ-rays) (Fig. 1 b). These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers. [3]



(a) (b)

Fig. 1 Design of Electron rays (a) and Design of Gamma rays (b)

The aim of this paper is to study the effect of ionizing radiation with different doses, on nano-mechanical properties of polyethylene and compare these results with those of non-irradiated samples. The study is carried out due to the ever-growing employment of this type of polymer.

Experimental

Material and methods

For this experiment High Density Polyethylene HDPE DOW 25055E, DOW - Chemical company, USA, (unfilled, HDPE) was used. The prepared specimens were irradiated with doses of 0, 33, 66 and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 420C. Processing temperature 190–220 °C, mold temperature 45 °C, injection pressure 70 MPa, injection rate 50 mm/s.

Nano-indentation test

Nano-indentation test were done using a Nano-indentation tester (NHT), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 20 N/min. After a holding time of 90 s at maximum load 10 mN the specimens were unloaded. A holding time was 21600 s at the creep. The specimens were glued on metallic sample holders. Poisson's ratio (ν) of the polymer was 0.3.

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (A_p) and the indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E^*) using an estimated sample Poisson's ratio (ν) according to: [4]

$$H_{IT} = \frac{F_{\max}}{A_p} \quad \text{and} \quad E_{IT} = E^* \cdot (1 - \nu_s^2) \tag{1}$$

Results and discussion

The figure 2 shows a very important correlation between the force and the depth of the indentation. The correlations provide very valuable information on the behaviour of tested material and the modified surface layer.

The correlation between the force and the depth of the indentation in HDPE also proved very interesting. It demonstrated the influence of radiation on the change of mechanical properties in the surface layer of specimens. The non-irradiated material showed low hardness as well as increasing impression of the indenter in the surface layer. On the contrary, the irradiated HDPE showed considerably smaller depth of the impression of the indenter which can signify greater resistance of this layer to wear.

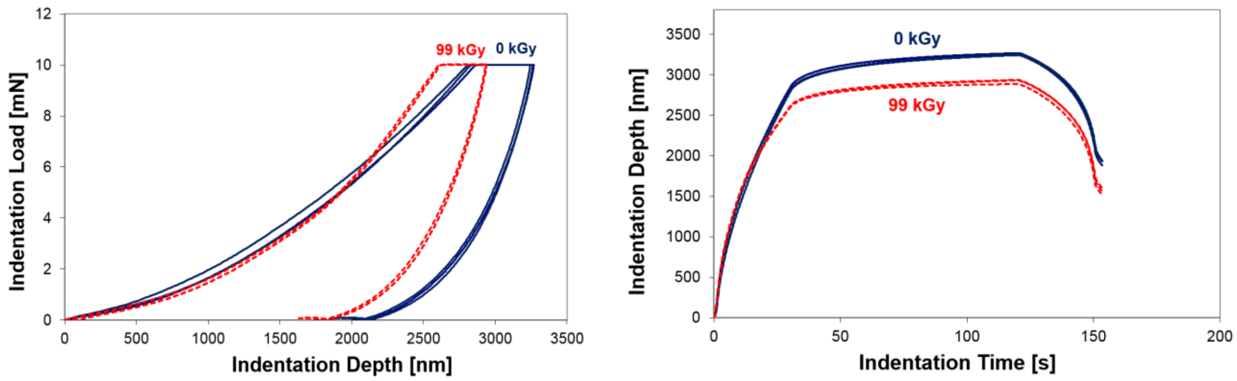
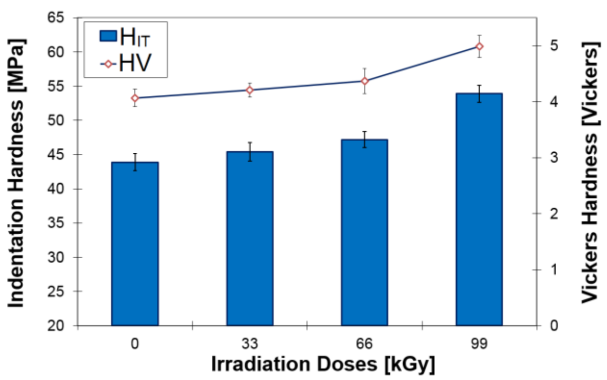


Fig. 2 Indentation characteristic of irradiated HDPE

The values measured during the nano-hardness test showed that the lowest values of indentation hardness and Vickers hardness were found for the non-irradiated HDPE. On the contrary, the highest values of indentation hardness and Vickers hardness were obtained for HDPE irradiated by a dose of 99 kGy (by 23% higher in comparison with the non-irradiated HDPE), as can be seen at Fig. 3.

According to the results of measurements of nano-hardness, it was found that the highest values of indentation modulus of elasticity were achieved at the HDPE irradiated with dose of 99 kGy (by 9% higher than compared with non-irradiated HDPE). On the contrary, the lowest values of the indentation modulus of elasticity were found for non-irradiated HDPE, as is seen at Fig. 4.



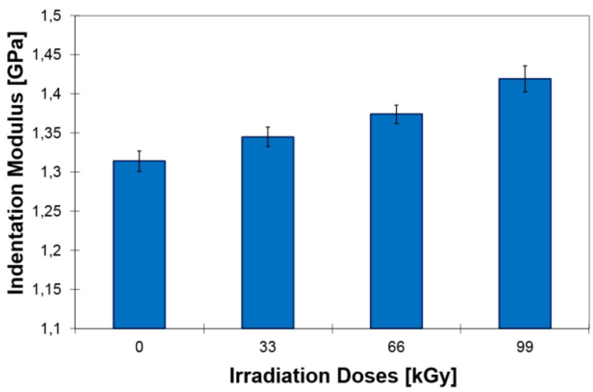


Fig. 3 Hardness vs. irradiation doses

Fig. 4 Indentation modulus E_{IT}

Very important values were found for indentation creep. Higher radiation dose influence significantly the indentation creep. An indentation creep increase of the surface layer is caused by irradiation cross-linking of the tested specimen. The lowest value of indentation creep was measured at radiation dose of 99 kGy. The highest indentation creep value measured at non-irradiated HDPE. Decrease in creep values was 29% for irradiated HDPE compared to the non-irradiated one as is seen at Fig. 5, 6.

Higher radiation dose does not influence significantly the nano-hardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the nano-hardness results reveals that when the highest radiation doses are used, nano-hardness decreases which can be caused by radiation induced degradation of the material.

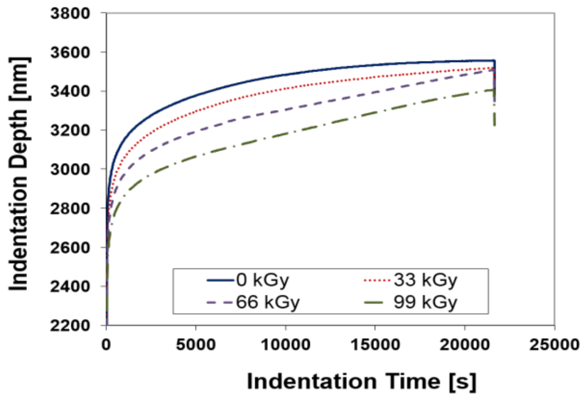


Fig. 5 Indentation curve (creep)

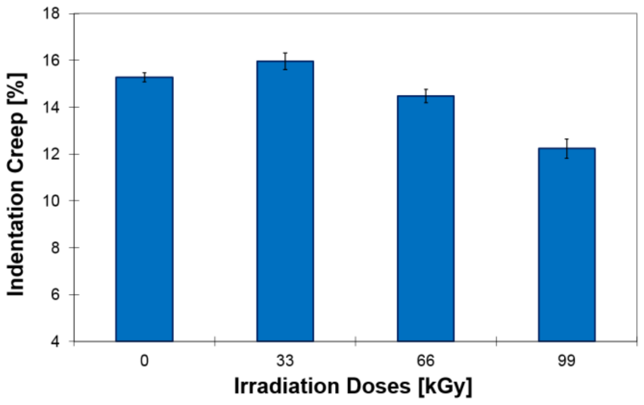


Fig. 6 Indentation creep of HDPE vs. irradiation doses

Conclusion

The article is the assessment of mechanical properties (nano-hardness) of the surface layer of modified HDPE. The surface layer of the polymer material such as HDPE is modified by β – radiation with doses of 33, 66 and 99 kGy.

The properties of surface layer of HDPE modified by beta radiation improved significantly. The nano-hardness values increased by about 23%. Stiffness of surface layer increased significantly by 10% as a result of radiation. The creep values decreased by 29% on average for irradiated HDPE. Also different depths of indentation in the surface layer of tested specimen were significantly different. The highest values of nano-mechanical properties were reached at radiation dose of 99 kGy. It also proved the fact that higher doses of radiation do not have very positive effects on the mechanical properties, on the contrary due to degradation processes the properties deteriorate.

The results of nano-mechanical properties of surface layer of modified HDPE show that it can be used in more difficult applications in some industrial fields, in particular where there are high requirements for strength, stiffness and hardness of surface layer which appears to be the most suitable area of application

Acknowledgment

This paper is supported by the internal grant of TBU in Zlin No. IGA/FT/2014/016 funded from the resources of specific university research and by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089 and Technology Agency of the Czech Republic as a part of the project called TA03010724 AV and EV LED luminaire with a higher degree of protection.

References

[1] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Hribova, K. Kocman, D. Samek, Irradiated Polypropylene Studied by Microhardness and WAXS, Chemicke listy, 106 (2012), 507-510.

[2] G. Zamfirova, V. Gaydarov, T. Zaharescu, L. G. Silva, Microindentation study of Electron Beam Irradiated Polyamide Samples, Chemicke Listy, 104 (2010), 283-286.

[3] D. Manas, M. Hribova, M. Manas, M. Ovsik, Stanek, Effect of Beta Irradiation on Morphology and Microhardness of Polypropylene Thin Layers, Thin Solid Films 530, (2013), 49-52.

[4] W.C. Oliver, G.M. Pharr, Measurement of Hardness and Elastic Modulus by Instrumented Indentation, Journal of Materials Research 19 (1), (2004), 1564 – 1583.

.